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An Evaluation of Dimethyl Ether as a Potential Solvent for the Extraction of Oil from Spent Coffee Grounds

ENG460 – Engineering Thesis

A report submitted to the school of Engineering and Energy, Murdoch University, in partial fulfilment of the requirements for the degree of Bachelor of Engineering

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Report by: Chris Sands
Unit Co-ordinator: Dr. Gareth Lee
Thesis Supervisors: Prof. Parisa A. Bahri & Dr Karne De Boer

Abstract

The world's dependence on fossil fuel based energy is causing major environmental and economic concerns. The need for environmentally friendly and sustainable fuel alternatives has been the driving force behind the recent advancements in biodiesel technology. However, the major battle that the biodiesel industry faces today is finding low cost and high quality oil feedstocks that will allow biodiesel to become economically competitive against fossil based diesel. One feedstock that could provide this solution is oil derived from spent coffee grounds. This work presents an alternative approach to the traditional hexane based Soxhlet extraction method by extracting oil from spent coffee grounds using Dimethyl Ether. The results obtained show extraction yields similar to those achieved by the standard hexane method. To analyze the quality of the extracted oil, different methyl esters constituents of the extracted oil were characterized using GC-MS techniques, identifying mainly C14 and C16 carbon chains. Mass and energy requirements of this process were determined by developing an Aspen Plus model from the results gathered during experimentation. A techno-economic assessment was performed to prove the economic feasibility of an industrial scale processing plant. The influence of temperature, rate of extraction and extraction efficiency should be investigated in future work. Moreover, to verify and validate the results obtained from the Aspen Plus model and techno-economic assessment, further development of the model and a detailed analysis is required.

Table of Contents

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1 Introduction

Due to the extensive growth in population and urbanization around the world, the demand for energy is increasing on a daily basis (Demirbas, Biodiesel - A realistic Fuel Alternative for Diesel Engines 2008). Despite the negative impact that climate change is having on our environment, the world's reliance on fossil fuels as its major source of energy is still evident (Administration 2013). On top of this, fossil fuel reserves are progressively decreasing and it is anticipated that they will be completely exhausted in the not too distant future, raising concerns for energy security (Jan C.J. Bart 2010). The consumption of fossil fuel based products, namely, petroleum and diesel, is largely contributed by the transportation sector, accounting for 63%. The carbon dioxide emissions that are released by the combustion of liquid fuels account for 34% of the world's total (Administration 2013). Various organisations (The American Association of State Highway Transportation and Intergovernmental Panel on Climate change) dedicated to the mitigation of climate change have proposed a range of solutions to reduce greenhouse gas (GHG) emissions. One solution presented to reduce emissions is to increase the use of fuels that produce minimal carbon dioxide, such as biofuels which are derived from renewable sources (American Association of State Highway and Transportation Officials 2012) (Change 2014).

Finding replacements for fossil fuels has been important since the oil crisis in the 1970s (Jan C.J. Bart 2010). With many countries now implementing strategies to increase their use of fuels produced from renewable sources and in turn reduce their reliance on imported fossil fuels, alternatives, such as biofuels, have gained an increasing amount of attention (The National Research Council 2011). The two main types of biofuels are bioethanol, a replacement for petroleum, and biodiesel, a replacement for diesel (Demirbas, Biodiesel - A realistic Fuel Alternative for Diesel Engines 2008). In recent years, the production of biodiesel has increased dramatically due to environmentally friendly nature and compatibility with existing diesel engines (S.P. Singh 2009) (Jan C.J. Bart 2010).

The term biofuels can be loosely defined as fuel, liquid or gaseous, derived from biomass materials, such as vegetable and animal matter (Biofuels Association of Australia 2014). The prospect of biofuels can be beneficial in numerous ways, for both developing and developed countries. With extensive accessibility to biomass sources, the biofuel industry could potentially provide more employment opportunities than the fossil fuel industry (Demirbas, Biodiesel - A realistic Fuel Alternative for Diesel Engines 2008). Furthermore, because biodiesel sources are completely renewable, it could be a potentially inexhaustible energy source that possesses energy content close to conventional diesel (Demirbas, Importance of Biodiesel as Transportation fuel 2007).

Although there are clear advantages to biodiesel, both economic and environmental, the rise of the biodiesel industry could result in direct or indirect negative effects to the environment (Lin Lin 2010). Biodiesel can be produced from a range of renewable oils and fats, which, in general, is largely depended on location (Tyagi 2006). The term feedstock refers to the unrefined fat or oil which undergoes the conversion into biodiesel. Currently, the most common feedstocks for biodiesel production are soybean oil (Palligarnai T. Vasudevan 2008), rapeseed oil (H. Chen 2010), palm oil (S.Mekhilef 2010), and Jatropha oil (Alok Kumar Tiwari 2007). In the presence of an alcohol, most commonly methanol because it's cost, oil or fat undergoes a chemical process known as transesterfication where the formation of esters, and byproduct glycerol, takes place (Palligarnai T. Vasudevan 2008) (Tyagi 2006). Also known as alcoholysis, the majority of biodiesel is produced using this method (Y.C. Sharma 2008) (Fangrui Ma 1999).

In an attempt to meet the requirements of their respective energy policies, there has been an increasing concern about the impacts on food prices and land change (M. Canakci 2001) (Lin Lin 2010). With a direct link between the issues just mentioned and the excessive price of vegetable oil, developments in agricultural yields or current technology must be made in order for biodiesel prices the be competitive with conventional diesel (Haile, Intergrated volarization of spent coffee grounds to biofuels 2014) (M. Canakci 2001) (Leandro S. Olivera 2007) (A.Deligiannis 2011) (Narasimharao Kondamudi 2008). For these reasons, the importance of oil feedstocks that are sourced from non-food crops is greater than ever for biodiesel to replace fossil based diesel (The National Research Council 2011) (Demirbas, Progress and recent trends in biodiesel fuels 2009). It has been reported that current feedstock's for biodiesel production can account for 70-85% of the overall processing cost (Jan C.J. Bart 2010) (Zayed Al-Hamamre 2012) (Antonio Zuorro 2011). Waste fats and oils present a cost effective solution to this problem. One waste oil feedstock which has proven to be a low-cost and high quality alternative is spent coffee grounds (Narasimharao Kondamudi 2008).

However, most of the waste feedstocks, including oil from spent coffee grounds, have high free fatty acid (FFA) and moisture contents (A.Deligiannis 2011). This characterization of FFA and moisture content has shown to result in a negative influence on the conversion from oil to biodiesel, by means of soap and gel formation. (Alok Kumar Tiwari 2007) (M. Canakci 2001). Moreover, the current methods of extraction, typically Soxhlet extraction with hexane, require the moisture content to be removed prior to oil extraction. This leads to excessive energy consumption and has hindered the process from being economically feasible (Haile, Intergrated volarization of spent coffee grounds to biofuels 2014) (Ricardo M. Couto 2009).

The aim of this work was to investigate an alternative method of extraction by employing the organic solvent, Dimethyl Ether. This method was anticipated to overcome shortcomings of current techniques by simultaneously removing the water and oil content from spent coffee grounds. To provide a comparison between the standard hexane based Soxhlet extraction and the Dimethyl Ether based alternative, experiments for both methods were performed. The outcomes from the Dimethyl Ether experiment showed promising results in terms of extraction yield with respect to the results achieved by the hexane experiment. Once both experiments had been conducted, the extracted oil samples from both methods were characterized for their different methyl ester constituents. However, due to the free fatty acids (FFA's) present in the oil, such as glycerol, an acid based transesterfication process was employed. This chemical process converts any FFA's into adequate derivatives, such as methyl esters, enabling the samples to be characterized by the GC-MS. Through this analysis, it was observed that the oil samples contained mainly C14 and C16 carbon chains. With the data obtained through the experimental work, an Aspen Plus model was developed in order to determine the mass and energy requirements of the system. The results generated by the Aspen model then enable sizing of the major equipment to be estimated based on the simulations performed. To evaluate the feasibility of an industrial scale extraction plant, a techno-economic analysis was also conducted using the information from both the experimental work and Aspen modeling.

2 Literature Review

2.1 Biofuels

Biofuels can be defined as liquid or gaseous fuels mainly derived from biomass for the use in transportation vehicles. In the realm of biofuels there are two primary classes, identified by the feedstock or production method, known as first and second generation biodiesels. First generation biofuels are those which have been produced from food crops. It is the vegetable oil or animal fat derived from these food crops that are used to produce biodiesel. The most frequently used first generation feed stocks are corn, sugar cane, and wheat (Biofuels.org.uk 2008). It is foreseen that the two main types of biofuels, bioethanol and biodiesel, will one day replace traditional petroleum and diesel fuels (Demirbas, Biodiesel - A realistic Fuel Alternative for Diesel Engines 2008).

2.1.1 Biodiesel

Although the use of vegetable oils as an alternative fuel source is increasing because of the depletion of fossil fuels, energy security, and climate change (Administration 2013), it is not a new technology. Originally designed to run on biomass sources (vegetable and animal fats), the compression-ignition engine was first invented by Rudolf Diesel in 1911 (L.C. Meher 2004). His first demonstration of the diesel engine showcased the ability to be fuelled from straight peanut oil; Diesel believed that this capability would enable the diesel engine to have long term viability. Although the use of vegetable oils to power the compression-ignition engine was still present during the 1930s and 1940s, it was generally in emergency situations and never held a prominent role. This was also due to petroleum products being cheap and in abundance at this time and therefore the diesel engine was more commonly modified by engine makers to suit petro-diesel instead (L.C. Meher 2004).

Due to its environmentally friendly nature, renewable biomass source and low emissions than petroleum diesel, biodiesel has become an attractive replacement for conventional diesel fuel (Fangrui Ma 1999). Furthermore, through the awareness of peak oil, depletion of fossil fuel reserves, and more recently the impacts of climate change, the use of vegetable oil or other biomass based fuels in diesel engines has returned. For these reasons, the use of biofuels, especially biodiesel, is being embraced more than ever by many countries (S.P. Singh 2009).The term biodiesel used to define the practice of using straight vegetable oils that would be used directly to substitute for diesel fuel. However, many inadequacies while employing it in this way were experienced and resulted in very few of these engines currently being used (Fangrui Ma 1999). The more recently used definition of biodiesel is to indicate fuels that are made up of mono-alkyl esters of long-chain fatty acids methyl ester (FAME) derived from vegetable oils or animal fats (Tyagi 2006) (M. Canakci 2001).

2.1.1.1 Production Technology

The most common method for producing biodiesel is the process of transesterification with an alcohol of vegetable oils and animal fats in the presence of a catalyst, either acid or base. Currently, there are two main types of transesterification processes for producing biodiesel. One technique employs a catalyst, such as a homogeneous, enzymatic, or heterogeneous catalyst, and the other uses a non-catalyst approach like supercritical processes (Aninidita Karmakar 2010). These methods for production, for what are known as first generation biodiesel, are subject to some serious issues. The necessary washing of glycerol and separation of catalyst from Fatty Acid Methyl Ester (FAME) processes have made a green product, biodiesel, currently experience a non-green process. It is due to the homogenous alkaline catalysts, such as sodium and potassium Hydroxide which require these

extra processing steps to occur. Another difficultly that presents itself is the high sensitivity to free fatty acids (FFAs) and water content in the oil source when using these catalysts. When alkaline catalysts react with FFAs, soaps and gels are formed, and results in the decrease of FAME yield and obscuring the glycerol separation. On the other hand, the presence of water in feedstock actually yields FFAs from FAME during the process of hydrolysis. Presence of FFAs and water content in feedstock should be lower than 0.5 wt. % and 0.06 wt. %, respectively. This then limits the production of biodiesel from these feedstocks when using the previous facilities for producing biodiesel with alkaline catalysts. As a result of these problems and the high price of vegetable oil, 80% of overall production expenses are just for the oil (R. Luque 2012).

The design and development of heterogeneous catalysts provide the biodiesel industry a challenge with prosperous advantages. Heterogeneous catalysts could refine the separation process, reduce the initial investment and decrease power consumption. This would optimize the process in terms of inputs, waste, soap and eliminate the need for catalyst. A higher quality of glycerol product could be obtained by eliminating the purification steps for neutralization products. Extensive research for biodiesel production has been conducted towards the progress of heterogeneous catalysts processes. Although some of these catalysts have exhibited good catalytic results, the implementation into an industrial application is still out of reach. This is because most of the experiments have been conducted in stirred batch reactors but a few continuous bed flow reactor processes have been carried out. In 2006, a revolutionary plant employing a unique heterogeneous process was established by Institute Français du Petrole (IFP), based on their Esterfip-H technology, capable of producing 200,000 metric tons per year. Although this technology has the potential to enhance biodiesel production, industrial scale applications require development of the mass and heat transfers. (R. Luque 2012)

2.1.1.2 Feedstocks for Biodiesel

With the rise in interest of biofuels, in particular biodiesel, a range of feedstocks have been investigated for fuel, ranging from edible oils, non-edible oils and animals fats. Examples of edible feedstocks are soybean, rapeseed and corn and non-edible sources include jatropha, waste oil and microalgae (Demirbas, Biodiesel - A realistic Fuel Alternative for Diesel Engines 2008) (Jan C.J. Bart 2010). However, with 80% overall productions expenses amounting purely from the feedstock oil, further investigation is needed to produce an economical product (R. Luque 2012).

Soybean oil as a feedstock for biodiesel production has grown in popularity in recent years, especially in countries like the US where soybean production is abundant. The US soybean production represents 40% of overall soybean output and for industrial applications, accounts for 50% of available bio based oil. The resultant fuel that is produced from soybean oil has shown some promising properties for the use in diesel engines, namely greater biodegradability, fewer emissions and increased lubricity. Although the process for biodiesel has been refined compared to other feedstock's, factors such as cold flow properties and oxidative instability have limited the utilization in northern parts of the world. It is anticipated that modification of soybean fuel properties by means of biotechnology tools will increase engine performance and make soybean crops progressively attractive as a feedstock (Palligarnai T. Vasudevan 2008).

Another feedstock which has been investigated recently is Palm kernels, with lipid content around 40%. Palm oil has been identified to have greater advantages compared with the more commonly

used rapeseed and soybean. Palm oil production is continuous and uninterrupted due to palm oil being a perennial crop. The oil yield from palm oil per hectare is the highest, yielding ten times more oil than that of rapeseed or soybean. Other advantages of palm oil include reduced water, pesticide and fertilizer require for the plantation. Although palm oil exhibits some of the best oil production characteristics, environmental factors including deforestation, endangering exotic animals and also food security have hindered palm oil from taking over as the dominant biodiesel feedstock (S.Mekhilef 2010).

To reduce concerning competition with the food industry and utilization of crop land, studies investigating the production of biodiesel from microalgae have shown some promising results. Various microalgae species yield different amounts of oil, some producing up to 50% oil yields by weight (Demirbas, Biodiesel - A realistic Fuel Alternative for Diesel Engines 2008). Microalgae requires minimal labor to grow and really only requires sunlight and some nutrients, enabling microalgae to grow almost anywhere. The growth cycles for microalgae are must faster than other sources, requiring only a few days to complete an entire growth cycle. Furthermore, the productivity and growth rates of microalgae are much higher in contrast to other agricultural crops and forestry, reducing amount of land area needed compared to other agricultural feedstocks. Unlike soybean or palm crops, microalgae species have the ability to adapt in various environmental conditions, making it feasible in most environmental scenarios. Currently, commercial scale applications for microalgae based biodiesel have not been undertaken, yet feasibility studies are currently underway to reach this goal (Teresa M. Mata 2009).

2.1.1.3 Biodiesel from Spent Coffee Grounds

The previously mentioned issues with common feedstocks are the limiting factors for biodiesel fuel to be competitive with traditional diesel. These, include, but are not restricted to, increasing food and land prices, deforestation and extinction of endangered animals (Leandro S. Olivera 2007) (Palligarnai T. Vasudevan 2008) (H. Chen 2010). Current feedstock's for biodiesel production account for around 70-95% of overall production costs (R. Luque 2012). Therefore, alternative feedstock's which produce high quality oil at a low cost need to be investigated in order for biodiesel to become economically viable (Narasimharao Kondamudi 2008) (Nidia S.Caetano 2012) (Leandro S. Olivera 2007).

One solution to help mitigate the current economic and environmental issues associated with biodiesel production is to use waste oils and fats as the feedstock. One of these waste alternatives is the oil extracted from spent coffee grounds and defective coffee beans. Coffee is one of the largest agricultural products produced due to this increase of consumption worldwide as a beverage. The rise in consumption has also led to an increase in the amount of waste coffee generated (A.Deligiannis 2011). The valorization of waste coffee grounds as a feedstock for biodiesel and other byproducts could offer an alternative waste management approach which could be environmentally and economically beneficial (A.Deligiannis 2011).

Depending on the species of coffee (Arabica or Robusta) the oil content ranges from 11-20% on a dry weight basis (Narasimharao Kondamudi 2008), which can be transformed into a comparable amount of biodiesel in the presence of an alcohol and aid of a catalyst via the trans-esterification process (Y.C. Sharma 2008). A number of recent studies have highlighted the benefits associated with the utilization of coffee grounds and beans. A study from the University of Nevada demonstrated that

the oil obtained from coffee is a higher quality and more cost-effective for the production of biodiesel than other waste oil sources and could possibly increase the world's biodiesel supply by 340 million gallons (Narasimharao Kondamudi 2008). A recent study from the University of Jordan investigated extraction methods by using polar and non-polar solvents; they reported that the best solvent for oil quality and amount extracted is the non-polar solvent hexane (Zayed Al-Hamamre 2012). This study also investigated the conversion of oil to FAME by experimenting with one and two step trans-esterification processes using potassium hydroxide in methanol solution. The two step process included a sulphuric acid in methanol solution pre-treatment to lower the free fatty acid (FFA) content. It was found that the two step process yielded 99% conversion of oil to FAME (Zayed Al-Hamamre 2012). Furthermore, the stability of coffee oil is better than other sources due to its naturally high antioxidant levels (Zayed Al-Hamamre 2012). Both of these studies used the Soxhlet extraction process with various solvents to achieve these results.

An alternative method to extract the oil from SCG is via supercritical fluid extraction (SFE) using CO2. In an attempt to validate an enhanced SFE method, a study from the Nova De Lis boa University in Portugal conducted a comparison between the Soxhlet and SFE extraction methods (Ricardo M. Couto 2009). This study considered the influence of operating conditions such as extraction time, temperature and pressure on the yield of oil and fatty acid profile. It was reported that the higher pressure and temperature conditions resulted in the highest extraction yield; a maximum of 15% (Ricardo M. Couto 2009). This is lower than the reported 18.3% obtained using the Soxhlet method and employing hexane as the solvent. However, with the addition on ethanol (6.5:93.5 w/w ratio) the extraction yield was increased to 19.4% on a dry weight basis (Ricardo M. Couto 2009). Although SFE could provide a more effective extraction process, the high temperatures and pressures make it an expensive process (R. Luque 2012).

The utilization of coffee grounds after extraction can be further used as fuel pellets or as a soil fertilizer or compost is also possible due to the nitrogen content present (Haile, Intergrated volarization of spent coffee grounds to biofuels 2014) (Nidia S.Caetano 2012). Moreover, another application that SCG is capable of is the production of bioethanol by the fermentation of sugars. This is possible due the amount of lignocellulose present. This bioethanol can then be used in the transesterification process to produce biodiesel from the lipid extracts from SCG (Jan C.J. Bart 2010).

2.2 Extraction Methods

Depending on the raw material available, the extraction may differ to suit its characteristics. A main contributor to depict the extraction method is moisture content. Raw materials such as seeds, beans and nuts have low moisture content, which require drying on harvest. Other raw materials such as palm, olive and coconuts are processed wet (Jan C.J. Bart 2010).

Although most oil (75%) is obtained from seeds, the processing to acquire this oil requires several transformation steps prior to extraction via organic solvents. In contrast, fruit oils such as avocado, olive and palm only require a couple of mechanical steps, and generally result in greater yields of oil per unit of area than oil seeds. The most common commercial processing of raw materials is described in the following subsections (Jan C.J. Bart 2010) (Kemper 2005).

2.2.1 Mechanical Extraction (Pressing /Expelling)

Oil (lipid) extraction via mechanical equipment has existed since 1795 (Kemper 2005) and can be achieved using two methods, pressing or expelling. This process is requires two stages, the forcing of oil and moisture out of the seeds, followed by the separation of desired product. In both cases, solvent extraction may also occur depending on the application and viability (Demirbas, Biodiesel - A realistic Fuel Alternative for Diesel Engines 2008).

A pressing machine, such as a hydraulic press, operates by applying pressure by means of a hydraulic plunger down onto a cylinder containing a batch of raw materials, forcing the lipids from the seeds, and resulting in a cake of pressed biomass (Kemper 2005). Solvent extraction is employed to further extract any lipids from the solid biomass (Jan C.J. Bart 2010). Olive oil extraction is the only industry which still employs hydraulic presses as there preferred method (Kemper 2005).

The screw press (expeller) performs oil extraction by depositing the biomass into a vertical feeder, which is then imparted with pressure by a horizontal screw. This horizontal screw follows the length of the surrounding barrel, which produced an increasing internal pressure that expelled the oil and biomass through to the end of the barrel. The major advantage to this design was that it enabled continuous oil extraction and process large amounts of biomass with minimal effort (Kemper 2005).

To achieve mechanical pressing of oleaginous seeds, several expensive pre-treatment stages can occur prior to processing. These include flaking, drying, cooking and de-hulling. These necessary procedures along with mass material storage and handling induce high operating costs for mechanical extraction (Jan C.J. Bart 2010).

2.2.2 Solvent Extraction

The term “Solvent extraction refers to the distribution of a solute between two immiscible liquid phases in contact with each other” (Michael Cox 2004). The description of the principle can be conceptualized in terms of a mixture containing two solutions initially dissolved together. One of the layers or phases will eventually distribute from the other after the solute has reached equilibrium. The fundamental principle is known as diffusion or dissolution. This physical phenomenon is achieved by refluxing a solvent through a solid material, such as biomass, for a known amount of time. The principle of solvent extraction is extensively used to extract lipids from vegetable and animal matter by using an extraction apparatus called a Soxhlet. This is the most common technique employed in industrial and laboratory experiments (Michael Cox 2004).

2.2.3 Supercritical Fluid Extraction (SFE)

Supercritical fluids (SCF) are not defined as a liquid or gas, yet they possess similar characteristics of both. For instance, SCFs matter is compressible and acts like a gas, unlike when it is in its liquid state. However, they have a density typical of a liquid and thus, possessing its characteristic liquid dissolving power (Dvoyashkin 2008). SCFs have some other important properties; they generate no liquid when a pressure change occurs or on solid surfaces, an increase in temperature will not form gas, the ability to continuously control density, polarity and viscosity over large variances in conditions and also, when small changes in pressure is experienced, especially around the critical temperature and pressure, the properties alter abruptly (Dvoyashkin 2008).

The technique of supercritical fluid extraction (SFE) can offer a viable alternative to the traditional and extensively used Soxhlet extraction. The capability to alter the dissolution power of a single

supercritical fluid by varying its density is an attractive feature. SFE could also provide a feasible alternative to other common sample preparation practices, such as liquid-liquid and, solid phase extraction (Joseph L. Hendrick 1992). This application SCF for extraction purposes have been around for two decades or more, including the decaffeination of coffee, black tea leaves, and also hop extract production (Ricardo M. Couto 2009). SFE processes are most commonly studied in the area of compound extraction from natural sources, with several hundred papers published (Ricardo M. Couto 2009).

There are a number direct advantages that SFE have over more traditional extraction methods; including continuous variation capability of the solvent control for SCF makes it a flexible process, facilitates the removal of poisoning organic solvents, and negates costly post-processing of products to separate from solvent (Marcelo M.R. de Melo 2013).

2.3 Hexane based Soxhlet Extraction

Hexane based Soxhlet extraction is the dominant method for extracting lipid content from organic matter. This is due to the amalgamation of its low cost, copious availability (due to hexane being a petroleum product) and extraction ability (ALAFFIA 2014). To perform this extraction method, hexane is refluxed in a special apparatus called a Soxhlet. The operation of this process follows these three stages.

1. Hexane is brought to its boiling temperature is a round bottom flask vaporizing the solvent into its gaseous state.
2. This hexane vapor will then travel up the apparatus through a condenser where it will return to its liquid state at the top of the Soxhlet.
3. The condensed hexane vapor then drips down into an extraction thimble containing the organic material, where a chemical interaction between the solvent and organic material removes the lipid content over time.
4. This process repeats until the lipid content is fully removed.

Hexane based extraction is used to extract oil for many different feedstocks for the production of biodiesel, including soybean, rapeseed, and palm. It has also been recently used to extract oil from spent coffee grounds, reporting oil extraction results from 11-20% on a dry weight basis (Narasimharao Kondamudi 2008) (A.Deligiannis 2011).

Although this method is the industry standard for such applications, excessive energy is required to continuously heat the solvent and toxic hexane fumes are often released into the environment (Suzana Ferreria-Dias 2003). Furthermore, this method requires large amounts of solvent and is also heavily depended on operational factors, including extraction time and cycles. In addition to this, hexane is a highly non-polar solvent; this then means that pretreatments to remove moisture from the particular materials are required to allow for this method to work. This additional pretreatment that employing hexane based Soxhlet extraction requires then leads to economic issues when applying this method on industrial applications (R. Luque 2012).

In an attempt to increase this methods extraction ability, techniques which involve polar co-solvents such as isopropanol have been investigated. This addition of a co-solvent does enhance the extraction yields of this method, however, separation of hexane and co-solvent from the desired

lipids then again adds additional steps to the process which require further energy consumption (Haile, Integrated Volarizartion of spent coffee grounds to biofuels 2014).

2.4 Oil Extraction Using Dimethyl Ether

Dimethyl Ether, the simplest Ether, is a synthetic fuel commonly employed as an alternative to LPG gas. Although most predominantly used as an aerosol propellant, Dimethyl Ether has also been investigated for the use as the working fluid in thermodynamic (Rankin) cycles. When compared to other organic fluids for this application, Dimethyl Ether presents a low cost and more effective option (U.S Department of Energy 2001).

In recent years, a number of scientific studies have investigated various applications of this organic compound. One of these applications is the dewatering of coal. Current methods for achieving this result proceed to consume large amounts of energy. Using a simple series connected 'once through' process, Dimethyl Ether has been proven to remove up to 98.3% of moisture from the solid coal material. This method does so by passing liquefied Dimethyl Ether through the coal in closed loop pressure regulated system. Once the water content has been removed by the solvent, a mixture of the water and Dimethyl Ether enters a separation vessel. This is where the main advantage to this process is identified. Due to Dimethyl Ether having a low volatility, it can be vaporized by simply exposing it to atmospheric temperature. This means there is no energy required to vaporize the solvent. Therefore opening a valve on the separation vessel vaporizes the Dimethyl Ether from the mixture, leaving only the water in the vessel. A further designed system which incorporated the recycling of Dimethyl Ether via compression and condensing was also investigated. This method was able to further reduce operational costs by reusing the solvent and only required energy to compress the vapor (H. M. Hideki Kanda 2010).

Further investigation into the possibility of this process has led to another study which performed the extraction of lipids (oil) from microalgae for biodiesel production. With the ability to simultaneously remove the moisture and lipid content from the micro algae, Dimethyl Ether provides an energy efficient alternative to the conventional hexane based soxhelt extraction process. Furthermore, negating the release of the toxic hexane fumes into the atmosphere, this method has environmental benefits (P. L. Hideki Kanda 2011) (P. L.-H. Hideki Kanda 2012). This then leads to using this method on various other organic materials for biodiesel feedstock oil which have high moisture contents.

3 Experimental Work

3.1 Introduction

This section of the report outlines the procedures and work done in order to complete the experimental aspects of the project. This includes performing the industry standard hexane experiment using a Soxhlet apparatus to facilitate a comparison between the alternative systems. A Dimethyl Ether experiment was then conducted and the results used to implement in to the Aspen Plus model. With both experiments completed an analysis of the oil extracted from both methods was achieved by esterifying the oil samples and employing commonly used GC-MS techniques.

3.2 Moisture Content for Spent Coffee Grounds Samples (SPG)

The moisture content of the SCG was determined by placing a sample of grounds in an oven over night at 50°C. The sample was weighed before and after.

$$\text{Moisture Content} = \frac{25.03\text{g} - 13.391\text{g}}{25.03g} * 100 = 46.50\%$$

3.3 Hexane Experiment

The technique of Soxhlet extraction is widely used in the chemical, pharmaceutical and food processing industries, but is most commonly used for the extraction of lipids (Christie 1989).

- 25.056g Sample (Dry Weight) – Experiment One
- 25.022g Sample (Dry Weight) – Experiment Two

Furthermore, research papers and recent studies have illustrated by means of thorough experiments, while taking into account the cost of the solvent, efficiency of extraction, percentage of oil yield and extraction time. Employing the solvent hexane will result in the highest level of extraction (Narasimharao Kondamudi 2008). Two experiments were performed to obtain a comparison between Hexane purity and the amount of oil extracted from the spent coffee grounds.

- Hexane (40-60) – Experiment One
- Hexane (60-80) – Experiment Two

Although the same solvent, both of these exhibit different boiling points due to their differences in purity. Hexane (40-60) boils at 69 degrees Celsius temperature range, as the name suggests, and similarly Hexane (60-80) boils between 60-80 degrees Celsius.

3.3.1 Equipment & Materials

- Electrothermal solid state mixer – For boiling the Hexane flask and continuous stirring.
- Soxhlet extraction apparatus with a distillation flask, water cooled double surface condenser attached – For the extraction thimble of coffee and condensing of Hexane vapor.

- Buchi water-bath B-480 and Rotavapor R-114 – This combination performs rotary evaporation under vacuum conditions to drop the boiling point of the substance to remove any excess hexane present.
- Two 28mm x 120 mm Cellulose extraction thimbles.
- 200mL of 40-60 Hexane and 60-80 Hexane.
- Two 25g samples of spent coffee grounds (SCG).

3.3.2 Experimental Procedure

3.3.2.1 Lipid Extraction

The experiment was performed under the supervision of organic chemist, Andrew Foreman, to ensure that health and safety standards were met, as well as to assist with operation of lab equipment.

Two Soxhlet extraction apparatus were setup, as illustrated in Figure 1. 200mL of Hexane was placed in the distillation flask at the bottom of both Soxhlet. 25g of spent coffee ground samples were placed in the cellulose thimbles and placed inside the Soxhlet. The following procedure was performed to achieve the extraction.

Procedure:

1. Firstly, the coffee grounds had to be dried to remove any excess moisture present in the samples, this can either be achieved by using an oven, or the leaving it out to dry in the sun. For the hexane experiment, the spent coffee grounds were left out in the sun for a day to remove any moisture content. However, to ensure that all moisture was removed, both samples were placed in an oven at 50°C for 4 hours.
2. A sample of coffee grounds (25g) was placed in the cellulose extraction thimble and inserted into the Soxhlet apparatus along with 200mL of hexane in the distillation flask.
3. Hexane is brought to 69 degrees Celsius, the correct boiling temperature, in the distillation flask to enable refluxing; the vapor rises up through the distillation path of the apparatus.
4. The hexane vapor floods into the chamber where the cellulose thimble containing the solid material is contained. Any vapor that does not go into the thimble chamber will travel above the expansion adapter and in will be cooled and condensed in the condenser back down into the chamber holding the solid material.
5. The warm hexane slowly fills the thimbles chamber and dissolves the lipid content of the coffee grounds, extracting the oil. When the thimble chamber is filled up to the siphon side arm, draining of the thimble chamber will occur automatically and empty back into the distillation flask.
6. The distillation flask will now contain a mixture of oil and hexane, due to the oil having a higher boiling point than that of hexane, the refluxing of hexane can continue with the oil present.
7. This process was repeated until the condensed hexane and extracted oil mixture at the bottom of the thimble chamber becomes clear, taking approximately 50 minutes.
8. The product mixture of Hexane and coffee oil will then be placed in a rotary evaporator to separate the desired oil from Hexane.

Figure 1 - Soxhlet Extraction Apparatus

3.3.3 Experimental Results & Analysis

The results of both experiments are displayed in Table 1.

Table 1 - Hexane Experimental Results

	Experiment One (40-60 hexane)	*Experiment Two (60-80 hexane)*
Duration of experiment	53 minutes	1 hour and 17 minutes
Sample weight (before)	25.056 g	25.022 g
Sample weight (after)	21.694 g	22.285 g
Thimbles filled	14 times	19 times
Amount of oil recovered	2.943 g	2.704 g
Oil Yield (%)	11.772 %	10.807 %

It can be seen in Table 1 that the results for experiment one proves to be marginally better than the results of experiment two. This was anticipated due to experiment one employing a purer form of hexane. Using a purer form of hexane means that the refluxing of the solvent will occur in shorter time due to the lower boiling point and hence reducing the extraction time. A difference of 24 minutes was observed between the two experiments to extract all the lipid content. This is due to

the thimble having filled 5 more times in experiment two. When taking into consideration that the duration of experiment two, it would be expected that the extraction yield would be greater.

However, this was found not to be the case and experiment one yielded almost 1% more oil than experiment two for the same amount of sample present. When calculating the results for both experiments, it was noticed that if the amount of oil extracted was compared to the difference between sample weight before and after, there was a small difference in weight. It is believed that this could be due the moisture content having not been completely removed during the drying process. Therefore it would be recommended that either the coffee grounds were left out in the sun for an extended period of time, or that an oven was employed to remove any moisture content; considering that the use of an oven would result in the most efficient drying technique.

In addition to this, when comparing the results to that of other studies published, both experiments yielded an oil content in the very low ranges. Most studies referred to in the literature review reported oil yields of 15.3 -21.5 wt. % when employing hexane or a mixture of isopropanol and hexane as the extraction solvent.

3.4 Dimethyl Ether Extraction

3.4.1 Experiment Trial

Prior to running a controlled experiment, a trial run was performed to ensure that correct system operation was achieved when a detailed experiment was finally conducted. Although the system did perform, this revealed some excessive cooling dissipation around the needle valve, which was greater than initially anticipated.

As DME expanded across the valve, flash evaporation of DME was experienced with an outflow mixture of liquid and vapor and some would stay liquefied as expected when considering the concept of a single stage thermodynamic cycle. This effect induced the freezing of the valve (Figure 3) and separation flask (Figure 2). To reduce this temperature drop across the valve, a length of copper tubing was wrapped around and tubing following it to create the effect of a heat exchanger. This did aid with the heating, however, it was not sufficient enough to prevent the valve from freezing over. Consequently a tube supplying room temperature air was placed underneath the valve, blowing ambient air on the valve. Although this did not completely eliminate the effect, it did mean that the valve remained unfrozen, allowing the operation to continue. The round bottom extraction flask was placed in a warm water bath to prevent the oil and water mixture from freezing. Furthermore, a water cooled condenser was used between the needle valve and flask to prevent any further DME from leaving the valve.

Figure 3 - Needle Valve Freezing

Figure 2 - Separation Flask Freezing

3.4.2 Experimental Apparatus

The experimental setup consisted of the following components:

- Storage cylinder which contained liquefied DME (9 kg of DME)
- The extraction column/vessel which contained the SCG samples and glass beads.
- Needle valve (thermal expansion valve).
- Water cooled copper tube heat exchanger.
- Water cooled double surface condenser.
- Pressure sensor.
- Water bath.
- Round bottom flask/separation vessel.
- Air cooling tube.

Wood supports were built to hold the DME cylinder and extraction vessel, ensuring that they did not move during operation. Figure 4 presents the experimental setup.

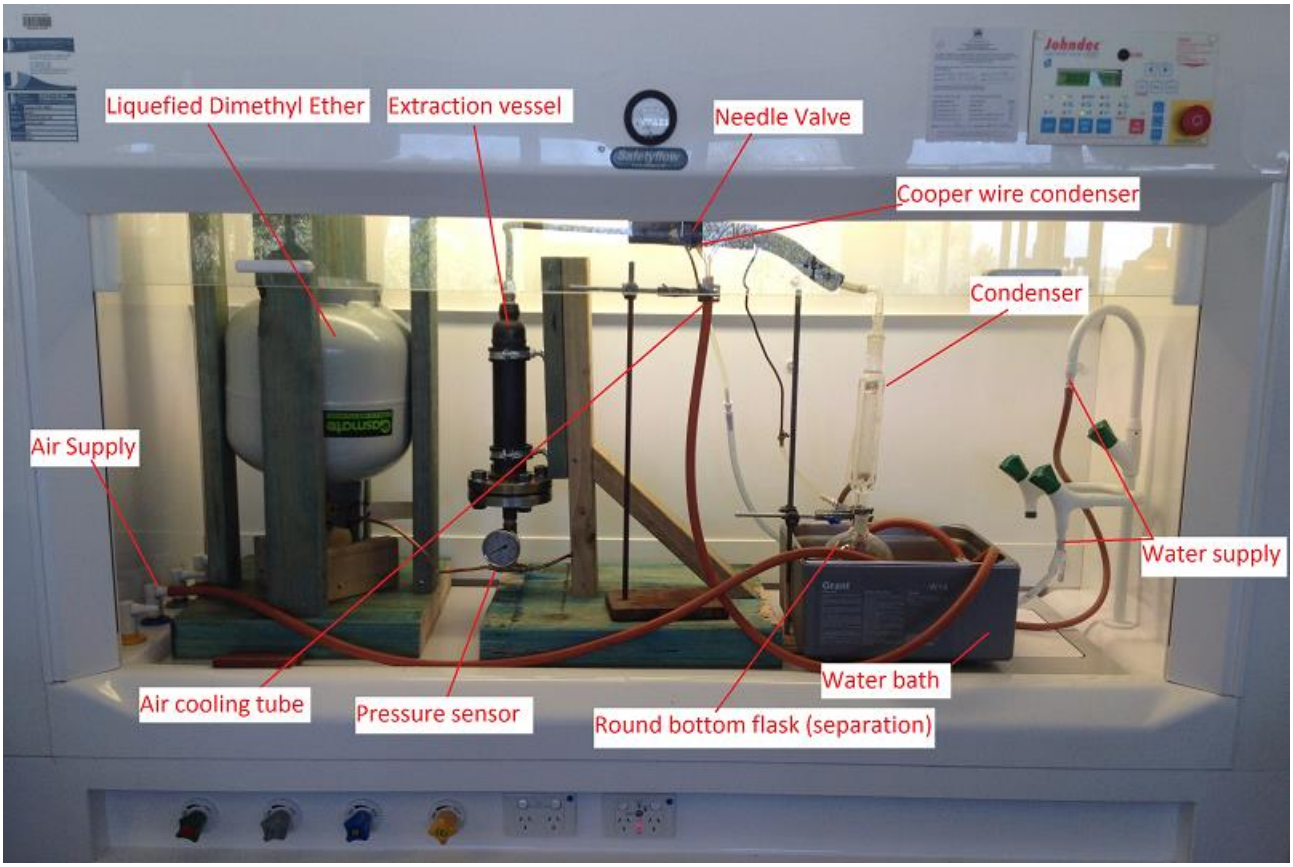

Figure 4 - Dimethyl Ether Experimental Setup

3.4.3 SCG Sample Preparation

Spent coffee ground (SCG) samples were obtained from a local coffee shop. Unlike the hexane extraction, these samples did not require the moisture content (42-46 wt. %) to be removed due to the de-watering ability that Dimethyl Ether (DME) possesses. Using a 250mL glass beaker and precision weighing scales, coffee samples were weighed.

- 211.8g sample in the 1st experiment.

- 204.9g sample in the 2nd experiment.

Prior to placing the weighed SCG samples into the extraction vessel, filter paper was placed in the column to minimize the risk of any solid material contaminating the product flow. With the filter paper in place, the measured SCG sample was placed in to the extraction vessel. Glass beads were packed on top of SCG samples to ensure the uniform distribution of the liquefied DME. Once this was achieved the extraction vessel was bolted together and ready for operation.

3.4.4 Extraction Process

Pressurizing the system was the first step of the procedure. While having the needle valve fully closed, the DME cylinder valve was fully opened, allowing liquefied DME to flow and charging the system up to the operating pressure (420 kPa). Once at the desired operating pressure, the needle valve was opened slightly. For approximately the first minute, depending on the percentage of valve position, any residual air that was present in the system was pushed through by the liquefied DME. When all the air was fully released, the noise of the system changed, identifying that liquefied DME had completely occupied the system.

By increasing the percentage of valve position, liquefied DME, water and oil (lipid content) started to flow through the valve. When passing through the valve an abrupt drop in pressure was experienced, the liquefied DME expanded as it was exposed to atmospheric pressure and a mixture of the DME liquid and vapor exited the valve. Once the mixture exited through the valve, it travelled through the water cooled condenser where room temperature water raised the temperature of the exiting stream, enhancing the vaporization of DME. Under gravity DME vapor travelled down into the round bottom flask where two outlets expelled any vapor removed via the fume cupboard. The water and oil mixture (containing a small amount of solid material) settled at the bottom of the flask and any residual liquefied DME present with the mixture slowly vaporized due to atmospheric pressure. The liquefied DME continued to remove any remaining lipid and moisture content from the SCG as it passed through the extraction column until the flow into the round bottom flask became clear, identifying that the lipid content had been fully removed. After this was observed, the liquefied DME flow was ceased by shutting off the valve. To depressurize the system, the needle valve was left open until atmospheric pressure was achieved; this may take up to an hour to complete with care being taken to avoid a surge in pressure.

3.4.5 Soxhlet Extraction of Residual Oil

After the DME extraction process was completed, Soxhlet extraction using Hexane was conducted to identify any lipid content remaining; the same procedure highlighted in the Hexane extraction section was followed.

During the extraction it became apparent that majority of the oil had been removed from the samples due to the observation that the color of the solvent in the thimble was only slightly tinged with yellow. Two 25g samples were taken from the residual solid material after extraction to determine whether all the lipid content was removed. It was found that experiments one and two resulted in a residual oil content of 0.049g and 0.057g respectively after one hour of Soxhlet extraction. It is expected that further development of the extraction design and optimization of the conditions will eliminate this residual oil content.

3.4.6 Experimental Results & Analysis

The results of both experiments are displayed in Table 2 below. It should be noted that the oil yield has been calculated on a dry weight basis.

Table 2 - Dimethyl Ether Experimental Results

	Experiment One	***Experiment Two***
Pressure	420 kPa	420 kPa
Sample weight (before)	211.8 g	204.909 g
Sample weight (after)	96.316 g	100.358 g
Dimethyl Ether Used	3.6 kg	5.4 kg
Amount of oil recovered	17.55 g	17.22 g
Oil Yield (Dry Weight) (%)	15.41%	14.64%
Moisture Content (%)	46.238 %	42.619 %
Residual Oil	0.049 g	0.057 g

The results of both experiments were analyzed and a comparison of the data highlighted that the second extraction produced better results in terms of the oil yielded when a smaller sample of coffee grounds were used. However, the second extraction consumed an additional 1.8 kg of DME. It is expected that this was most probably due to the DME flow rate that was achieved in the second experiment. Once confident with the process operation the author realized that increasing the valve position gradually over time meant that a larger flow rate could be achieved without experiencing an abrupt surge in pressure. The moisture content of both samples was calculated after extraction by subtracting the weight of the oil recovered and the weight of the residual coffee grounds from the original sample weight. This resulted in a moisture content of 46.238 wt. % for experiment one and 42.619 wt. % for experiment two. When compared to the sample of coffee grounds that was dried in the oven at 50°C over night without undergoing extraction, which was 46.5 %, it had been assumed that all moisture content had been removed by the DME extraction process. This was verified by placing the 25g of each experiment sample into the oven under the same conditions. After the samples were removed from the oven and reweighed, the difference was considered negligible.

In comparison to the hexane experiments performed and other studies presented in the literature review, the results obtained were quite significant. To achieve such high oil yields (17-19 wt. %) from an experiment with no optimization or process control implemented. Furthermore, Dimethyl Ether's inherent ability to remove moisture (de-water) while simultaneously extracting oil, will result in a reduction in the amount of energy that is required by the process. Although the pressure of the system in quite high (420 kPa), it is significantly less than that of supercritical fluid extraction (SFE). As mentioned in the literature review, SFE with the aid of methanol as a co-solvent exhibits an oil yield of 19.4 wt. %. However, very high extraction temperature and pressures have hindered SFE

from being an economical alternative to the conventional Soxhlet methods. With the hexane experiments performed in this project accomplishing low oil yields (10-11 wt. %) and other reported yields between 11-21.5 wt. % from a range of organic solvents, Dimethyl Ether, in terms of extraction ability, could be considered an alternative to conventional solvents. Although hexane is also low cost and in abundance, this alternative method using Dimethyl Ether recycles the solvent throughout the process which will greatly reduce the amount of compared to using hexane in the standard Soxhlet extraction.

Overall the Dimethyl Ether experiments have produced some significant results. With further development into a continuous system, reducing the amount of Dimethyl Ether used and optimization of the operating conditions, this method of extraction has the potential to replace existing extraction plants.

3.5 Washing and Evaporation

After the extraction mixture had been obtained, it was necessary to perform a washing and evaporation process to ensure that all of the organic solution had been recovered. To obtain any residue left behind in the glass condenser, hexane (2*40mL) was washed through into a beaker. The same process was performed for the oil collected in the round bottom flask. The residual oil and product oil are placed into a separation funnel and mixed thoroughly to ensure that the organic and aqueous phases equilibrate. While shaking the mixture in the flask, the pressure was released continuously to avoid excess pressure building up in the separation funnel (Figure 6). Once the aqueous and organic solutions had split in to their respective phases in the separation funnel, the aqueous solution was removed carefully into a glass beaker via the stopcock to ensure that no organic solution was removed (Figure 5). The organic phase was then removed and placed into a round bottom flask and the same procedure was carried out on the separation funnel.

Figure 6 - Evaporation Process

Figure 5 – Separation Process

The hexane used to rinse the round bottom flask was removed via evaporation, which was achieved by using a rotary evaporation (Figure 8). Once all the hexane had been removed from the solution, the remaining oil in the bottom of the flask was weighed to determine the percentage of oil yield. Figure 7 shows the recovered oil after rotary evaporation. The oil was then ready for further refining for use in the gas-chromatograph; this process is called esterification or also commonly known as the technique of Derivatization.

Figure 7 - Rotary Evaporator

Figure 8 - Extracted Oil

3.6 Derivatization/Esterification

To enable the analysis and identification of compounds present within the oil extracted, Gas chromatography practices were employed. However, straight oil contains free fatty acids and other compounds which require conversion to adequate derivatives, like methyl esters, in order to facilitate GC methods (Christie 1989). To achieve this conversion, a process known as derivatization was applied.

The fundamental concept behind derivatization is fostering the reaction between an alcohol (typically Methanol) and a fatty acid, in the presence of a catalyst. Different methods can be employed depending on the lipids being converted, with either an acid or alkali catalyst being utilized (Christie 1989). A study conducted at Ohio University investigated the extraction of lipids from microalgae, in this study both an acid and base catalyst esterification process were employed. However, the results from these derivatization methods were unreliable and implemented unsuccessfully (Anthony 2010). However, an acid catalyst esterification and transesterification method proposed by (Christie 1989) proved to be more reliable and produced better results.

Procedure:

Using a test tube with an attached condenser, a lipid sample (up to 50g) was dissolved using 1 mL of toluene prior to adding 2 mL of methanol with 1% of sulfuric acid. The test tube was then sealed and a temperature 50 degrees Celsius maintained overnight. 5 mL of water containing 5% of sodium chloride was then added and thoroughly mixed (Christie 1989). Glycerin and other water soluble compounds were dissolved, leaving a mixture that was separated into an aqueous and organic phase

(Anthony 2010). Once the organic phase was removed using a pipette, a known amount of hexane was added to extract the required esters.

The lipids which are non-polar and cannot be dissolved in methanol based solvents were dissolved using toluene. Historically Benzene was the preferred solvent used to dissolve the lipids, but due to the fact that toluene has a lower toxicity, it has now replaced benzene as the standard solvent (Christie 1989).

3.7 Gas-Chromatography & Mass Spectrometry (GC-MS)

This technique of Gas-chromatography (GC) is fundamental to the separation of lipids from organic compounds, particularly their fatty acid constituents, and is one of the major reasons that such an wealth of knowledge about these natural products is existent today (Christie 1989).

Gas Chromatography has three essential components; the sample injection inlet, the column and a detector. The inlet allows the sample to enter the column either manually or via an auto sampler. The column contains the stationary or liquid phase which is continuously passed by the mobile or gas phase. The detector monitors the outlet stream, identifying the time each component reached the outlet and amount of that component. Once the sample has been injected into the system an inert gas, like helium, passes through the system and transports the sample into the column. In this column (which is layered with the stationary or liquid phase) the interaction between the samples brought through by the carrier gas and the stationary phase then results in the separation of the sample compounds (Christie 1989). Depending upon the particular compounds degree of interaction with the stationary phase, separation of each molecule is then identified by the various times in which they leave the column and enter into the detector (Anthony 2010). An electrical signal is then generated by the detector from a conversion of the components concentration, which then passes through a continuous recorder after amplification of the signal (Christie 1989).

Although GC is a useful technique, it does result in a level of ambiguity. The detection of separated compounds is dependent upon the retention times in which they leave the column. Therefore, when compounds with very similar retention times are present, it becomes very difficult to identify which compound is associated with its respective retention time. To minimize this degree of uncertainty an additional technique called Mass-Spectrometry (MS) is used in conjunction with GC. Although MS is rarely used for detection, it is an invaluable tool when attempting to identify separated lipids (Christie 1989).

The MS technique works by forming positively charged ions from the electrons being propelled at the organic molecules present in the vapor phase, these ions are then separated in relation to their mass to charge (m/z) ratio by passing them through a magnetic (or electrostatic) field (Christie 1989). As the mass to charge (m/z) ratio increases, the fragmented compounds or ions are collected in sequence. An intensity value of 100 is assigned to the base or highest peak in which all other ions intensities are normalized. With the use of high resolution instruments, the accuracy of measuring individual ion masses is sufficient enough to determine the molecular formula (Christie 1989).

Mass spectrometry is a reliable tool when identifying single molecules samples, however, when samples contain various components it becomes less effective (Anthony 2010). Consequently the use of the MS method with GC has been widely implemented. The separation of component

mixtures relative to their molecular weight achieved through GC has meant that there is a method that allows for the effective successive analysis by mass spectrometry (Anthony 2010).

3.7.1 Procedure & Analysis

Using a Shimadzu GCMS-QP2010S system, an analysis of the lipid samples was performed. The method used is detailed in Table 3. The oil samples which have undergone the esterification process previously described were analysed for the Fatty Acid Methyl Ester (FAME) content. 200µL of the organic phase from each of the samples was removed and diluted with 800µL of hexane in a GC vial.

Table 3 - GC-MS Method

Parameters	Values
Column Oven Temperature	80.0°C
Injection Temperature	250.0°C
Sampling Time	1.00 min
Flow Control Mode	Linear Velocity
Pressure	61.7 kPa
Total Flow	99.8 mL/min
Column Flow	0.96 mL/min
Linear Velocity	36.1 cm/sec
Purge Flow	3.0 mL/min
Split Ratio	100.0
Oven Program Initial Temperature	80°C
Hold Time 1	5 min
Temperature 2	240°C
Hold Time	30 min
Temperature Final	250°C
Hold Time	10 min

C17 (methyl heptadecanoate) and FAME standards were purchased from Sigma-Aldrich to identify FAME retention times and were also used to spike the esterified oil. Firstly, the 1 mL of FAME standard was mixed with 10 mL hexane to create a standard with a known concentration (1/11 ratio). This standard was used to work out the different retention times of different FAME constituents. Then 0.103 g of the C17 standard was mixed with hexane in a 10 mL volumetric flask but with a 1/10 ratio. This 1.03% C17 in hexane standard was then used to spike the esterified oil to enable the proportions of fatty acids present in the oil to be calculated. The organic phase and

hexane samples that were originally in the GC vials where spiked with 400µL of the 1.03% C17 standard in new GC vials ready to be run through the GC-MS.

After all the samples were run through the GC-MS, reports of each sample were produced and analyzed. Using these reports from the FAME standard, the spiked esterified oil samples retention times were compared. The results of the oil extracted from both hexane and Dimethyl Ether showed that large amounts of myristic acid (C14) and palmitic acid (C16) were present, but that only small amounts of oleic acid (C18.1) were existent. These methyl ethers are what should be expected to be found in the oil according to other studies of spent coffee ground extraction, but other methyl esters such as linoleic (C18.2) and stearic acid (C18) were not evident. It is believed that the GC-MS runs that were performed had not generated the correct retention times for the methyl ester continents present in the oil. In order to accurately identify the retention times of the different methyl esters in the FAME standard and correlate those retention times and the percentage of them present with the results of those obtained from the extracted oil samples, a refined GC-MS method needs to be achieved. Due to the time constraints of the project, this was not possible to accomplish but instead will be one of the objectives that will be highlighted for future work.

4 Aspen Plus Model

To refine the design, operation and optimization of the extraction process investigated in this project, an Aspen Plus model needed to be developed. The design of this system is very similar to that of a typical continuous thermodynamic refrigeration system, including an evaporator, condenser, expansion valve and compressor (Figure 9). After conducting the Dimethyl Ether extraction experiment on a laboratory bench scale, the amount of solvent required to extract a specified amount of solid material was obtained. With this information and on the basis of 10,000 tons a year of spent coffee grounds being available, a flow rate of Dimethyl Ether (25.678 tons/h) can be implemented into the model. This will allow the material and energy balances and power requirements of the system for the compressor, evaporator and condenser to be calculated. This information is invaluable when performing the techno-economic analysis.

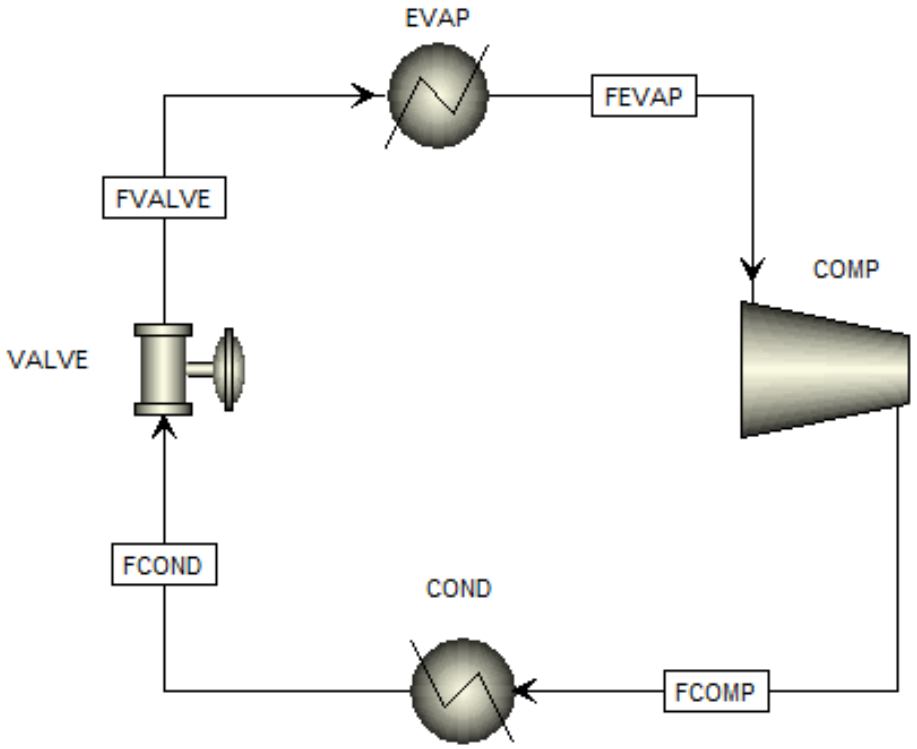

Figure 9 - Aspen Plus Simulation Flow Sheet

4.1 Model Operation

As mentioned above this model does not include the solvent extraction chemical process of the spent coffee grounds by Dimethyl Ether, nor the separation of mixture into Dimethyl Ether vapor and oil and water in the evaporation vessel, but the operation of other components in terms of energy that can still be obtained. After the extraction of lipids (oil) from the solid material has taken place, the oil, water and liquefied Dimethyl Ether needed to be separated. This modeling aspect was achieved by using a throttling or thermal expansion valve at the entry of the evaporation vessel. An abrupt pressure drop over the expansion valve (4.4 bar) was experienced by the mixture prior to entering the evaporation/separation vessel. The exposure to atmospheric pressure makes Dimethyl Ether to expand and partially vaporize from the oil and water present in the mixture. The specifications of the valve were set to a vapor fraction of 1. The model assumes that the Dimethyl

Ether is completely in vapor form. However, in a typical single stage thermodynamic (vapor compression) refrigeration cycle, this abrupt pressure reduction of the liquid refrigerant over the thermal expansion valve results in what is known as an adiabatic flash evaporation of a percentage of the liquid refrigerant. The flash evaporation process reduces the temperature of the liquid and vapor mixture to the extent that the temperature of the vapor and liquid mixture is lower than that of the enclosed space to be refrigerated. This then confirms that the process has experienced the refrigeration cycle operation because the temperature of Dimethyl Ether vapor-liquid mixture at the valve outlet is 13.7 °C. At this temperature, Dimethyl Ether could not theoretically be a complete vapor. The mixture of vapor and liquid Dimethyl Ether will then enter the evaporation stage. In a real continuous system this evaporation process would happen inside the evaporating vessel where the liquefied Dimethyl Ether would separate from the oil and water mixture through vaporization. However, due to the actual extraction of oil and water from the spent coffee grounds not being present, it was not possible to model this at this point in time. A heat exchanger was therefore used to determine the amount of energy absorbed/removed by the change in state from Dimethyl Ether as a pressurized liquid into its natural gas/vapor form.

In the evaporator, any residual liquefied Dimethyl Ether should be vaporized, and theoretically the oil and water content in the mixture should settle at the bottom of the vessel and be removed as the product. The temperature of the Dimethyl Ether at the outlet of the evaporator unit is now at the saturation temperature (boiling point) of Dimethyl Ether, -24.872 °C. This would suggest that during the evaporator stage all liquefied Dimethyl Ether has vaporized. This evaporator heat duty is modeled to be -1365.82 MJ/h. The heat duty is negative because heat is being rejected from the system. Although this does seem quite excessive, considering a flow rate of 28.687 tons/h running through the system and how extensive the temperature and pressure changes are when the Dimethyl Ether expands, this is assumed to be viable. According the Aspen Plus model results for this stage, a 379.394 kW heat exchanger would be needed to achieve this in a real world continuous system.

As mentioned above, this model assumes that all Dimethyl Ether has vaporized after leaving the evaporator. As a typical thermodynamic cycle for a refrigeration system would operate, the circulating refrigerant is in the thermodynamic state called saturated vapor. This saturated vapor is then mechanically compressed to pressurize the system back up to the required vapor pressure, allowing the Dimethyl Ether to be liquefied again. The energy required to compress the Dimethyl Ether up to 5.413 bar also causes the temperature to increase to 59.79 °C. As a result the hot compressed vapor is in a thermodynamic state referred to as a superheated vapor. This isentropic compressor mode is also based upon the assumption that the vapor fraction is 1, which relates to how the single stage vapor compression cycle would operate. The results for the compressor model in Aspen Plus identify that to achieve this pressure increase, the net-work produced by the compressor would be 795 kW.

After the Dimethyl Ether vapor has been recompressed, it is now at a current pressure and temperature which allows for the vapor to be condensed with either a water or air cooled condenser. This is achieved in the Aspen plus model by using another heat exchanger. The Dimethyl Ether vapor flows through the condenser whilst removing the superheat generated by the compressor and therefore cooling the vapor. As it flows through the rest of the condenser, the cooled vapor is condensed into to a saturated liquid. The operation pressure should remain fairly

constant during this process; this was confirmed by the outlet temperature of the model results being 5.413 bar. The condenser reduces temperature of the stream from 59.79 °C, to 21.996 °C. This condenser requires a net-duty of -1496.28 MJ/h (-415.63 kW) to achieve the following results. Condensers remove heat from a process and hence the net-duty is negative. The energy balance, pressure and temperature for each of the components are illustrated in Table 4 below.

Table 4 - Aspen Plus Simulation Results

	Energy balance	***Pressure***	***Temperature***
Compressor	796 kW	5.413 bar	59.791 °C
Condenser	-417 kW	5.413 bar	21.999 °C
Evaporator	-379 kW	1.0135 bar	-24.872 °C
Valve	N/A	1.0135 bar	13.726 °C

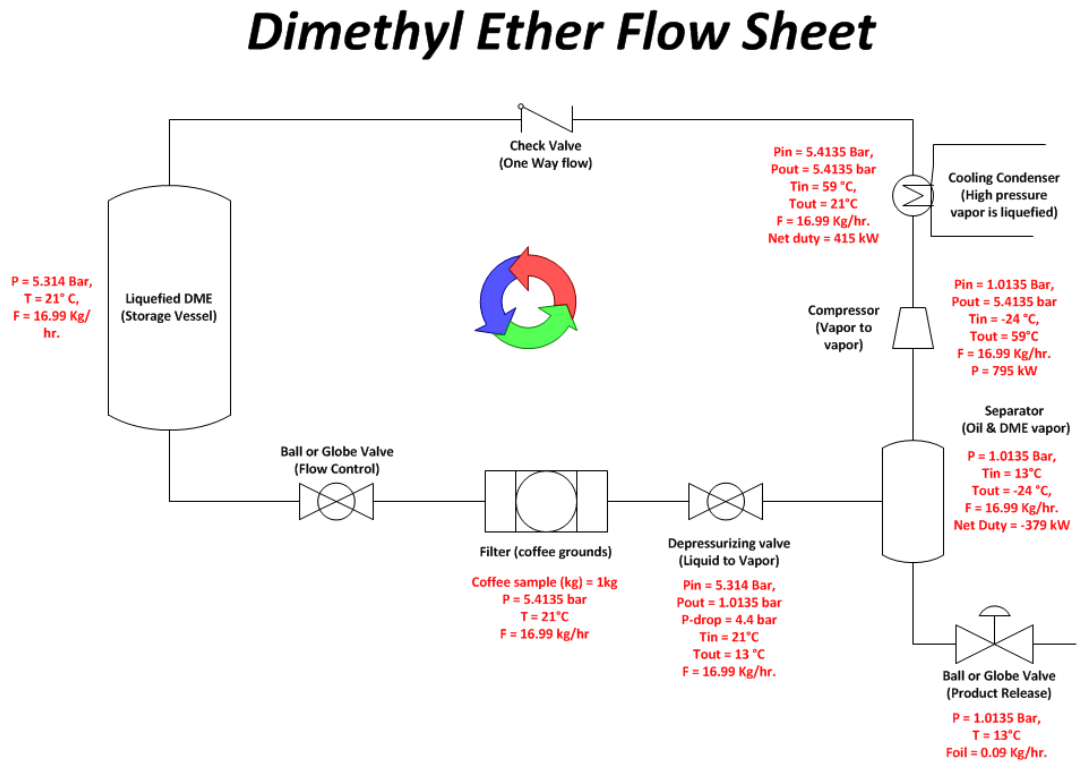

Figure 10 - Preliminary Continuous Flow Sheet Design

With results from both the Dimethyl Ether experiment and Aspen model, a continuous process flow sheet was able to be developed. The flow sheet in Figure 10 illustrates the design that would have been constructed with the addition of the operating conditions and absorption/ rejection requirements of the evaporator and condenser. This will be required in the later stages of the project when a techno-economic assessment is undertaken and a continuous experiment is designed.

5 Techno-Economic Assessment

To prove the economic feasibility of the investigated extraction system on an industrial scale, a preliminary techno-economic analysis has been performed. The extraction plant will be based on a plant capacity of 10,000 tons of spent coffee grounds per year. Following the factorial method (Lang Factor) described in (Sinnot 2005) a cost estimation of the extraction plant has been obtained. The procedure estimates the total investment required for this project according to (Sinnot 2005) is detailed below:

- Formulate material and energy balances, develop a preliminary flow-sheet and roughly size major equipment.
- Obtain the major equipment cost (PCE) and the physical plant cost (PPC), using direct cost factors in Table 6 in Appendix C.
- From the direct cost factors, determine the indirect costs from Table 5. Total fixed capital is determined by both direct and indirect costs.
- Determine the working capital, generally 10-20 % of the fixed capital cost.
- The addition of working and fixed capital leads to the total investment necessary (Sinnot 2005).

Using the procedure outlined above, an estimation of the total investment necessary to construct and operate the extraction processing plant described in this project has been performed. The material and energy balances in Table 4 and the preliminary flow sheet in Figure 10 have been determined by the Aspen Model detailed previously. The next step is estimate the cost of purchasing the major equipment. It should be noted this is a rough estimation done using the information provided in Table 6 (Sinnot 2005).

Using these assumptions will allow the total investment required to be estimated. Now using substituting the values present in Table 6 in *Appendix C,* the total cost of equipment can be estimated. All equipment calculations can be seen in *Appendix C.*

Using the cost estimations for each piece of equipment and adding them together, the total cost of major equipment is (Sinnot 2005):

$$PCE = \$507{,}503.672$$

To acquire a more detailed factorial estimate, including direct and indirect costs, additional cost factors should be included into the original “Lang Factor”. The direct cost factors also include those costs that pertain to the construction of a processing plant in addition to the major equipment costs and are outlined below (Sinnot 2005):

1. *Equipment erection*
2. *Piping requirements*
3. *Electrical consumption*
4. *Instrumentation*
5. *Process buildings/structures*
6. *Ancillary buildings*

7. *Storage of materials and products*
8. *Utility services*
9. *Site and preparation*

These factors Table 5 - Direct & Indirect Cost Factors contribute to the capital cost by multiplying the suitable Lang factor by the total equipment cost. In addition to these direct cost factors, there are also indirect cost factors that are accounted for below:

- ***Design and engineering*** – These incorporate the purchasing, procurement and erection of the plant. Generally this amounts to 20-30 % of the total capital costs.
- ***Contractor's fee's*** – The contractors profit (fees) will be in addition to total capital costs, generally 5-10 %.
- ***Contingency costs*** – These are incorporated to allowance for any unforeseen issues associated with the construction of a plant, usually 5-10 % of the direct costs (Sinnot 2005).

Table 5 - Direct & Indirect Cost Factors (Sinnot 2005)

Item	Fluids	Fluid-solids	Solids
Major Equipment Cost, Total purchase cost	Purchased Cost Equipment (PCE)	Purchased Cost Equipment (PCE)	Purchased Cost Equipment (PCE)
-Equipment erection	0.4	0.45	0.50
-Piping	0.70	0.45	0.20
-Instrumentation	0.20	0.15	0.10
-Electrical	0.10	0.10	0.10
-buildings, process	0.15	0.10	0.05
-Utilities	0.50	0.45	0.25
-Storages	0.15	0.20	0.25
-Site Development	0.05	0.05	0.05
-Ancillary buildings	0.15	0.20	0.30
Total	**3.40**	**3.15**	**2.80**
Indirect Costs			
-Design and Engineering	0.30	0.25	0.20
-Contractors fee	0.05	0.05	0.05
-Contingency	0.10	0.10	0.10
Total	**0.45**	**0.40**	**0.35**

To incorporate these direct and indirect cost factors the following equations for Physical plant cost (PPC) and fixed capital are used:

$$PPC = PCE \times (1 + f_1 + f_2 + \cdots f_9)$$

The extraction processing plant of interest in this project would be a combination of fluids and solids; therefore a multiplication factor of 3.15 is used.

$$PPC = \$507{,}503.672 \times 3.15$$

$$PPC = \$1{,}598{,}636$$

With the direct cost factors now combined, the indirect cost factors can now be incorporated.

$$Fixed\ Capital = PPC \times (1 + f_{10} + f_{11} + f_{12})$$

Again, using the total combined factor of indirect costs for fluids-solids processing plant, of 1.40, the equation becomes:

$$Fixed\ Capital = \$1{,}598{,}636.56 \times 1.40$$

$$Fixed\ Capital = \$2{,}238{,}091$$

With the total fixed capital now calculated, the working capital can now be estimated. On the assumption that the working capital is 10% of the fixed capital, the working capital would be (Sinnot 2005):

$$Working\ Capital = \$2{,}238{,}091.194 \times 0.10$$

$$Working\ Capital = \$223{,}809$$

Total investment required for this project can now be determined by adding the working and fixed capitals together, resulting in a total investment of (Sinnot 2005):

$$Total\ Investment = \$2{,}238{,}091 + \$223{,}809$$

$$Total\ Investment = \$2{,}461{,}900$$

Once an estimate of the total investment for the project has been calculated, the operating cost of the system can be determined. In order to prove the validity of the project, the expense of producing the product must be incorporated. Operating costs can be split into two factors, fixed and variable costs. Fixed costs are those which are essential to overall operating and do not fluctuate with production rate. Variable costs of the other hand are directly depended to the quantity of production. (Sinnot 2005)

Fixed Costs:

- Maintenance
- Operating labor
- Laboratory costs

- Supervision
- Plant overheads
- Capital charges
- Rates
- Insurance
- License fees

Variable Costs:

- Raw materials
- Miscellaneous operating resources
- Utilities
- Shipping and packing (Sinnot 2005)

The raw materials that are required for this process are Dimethyl Ether and spent coffee grounds. It has been determined through experimentation that 16.99 kg of Dimethyl Ether is required to extract 1 kg of spent coffee grounds. Then, on the basis that the plant will run for 7 days a week, 24 hours a day and for 50 weeks of the year, the amount of Dimethyl Ether required to extract 10,000 tons of spent coffee grounds is 169,900 tons of Dimethyl Ether. At $1.50 per kg (for copious quantities), the annual cost of extraction solvent is $254,850. However, due to the system recycling the Dimethyl Ether during operation the cost of raw materials is not included in the assessment. Presently spent coffee grounds are a waste product from the consumption of coffee as a beverage, and therefore the cost of the spent coffee grounds as a raw material is zero.

Utility costs for annual plant operation is a variable cost that is dependent upon the production rate of the process; as this is system is made up of components that consume electrical and water, these are the only utility costs that are included. Based upon the cost of electricity ($0.245961 per kWh) and water charges ($2.730 per kL) relative to plant location, the following utility costs have been roughly estimated.

$$Water\ costs = \$16{,}380$$

$$Electricity\ costs = \$1{,}174{,}418$$

$$Total\ Utility\ costs\ = \$1{,}235{,}682$$

Generally, chemical processing plants do not require a large workforce to maintain and operate the plant. On this basis it has been assumed that three employees on an annual salary of $80,000 would be required (Sinnot 2005).

$$Operating\ Labor = \$240{,}000$$

Using factors illustrated in Figure 21 in *Appendix C*, the remaining fixed and variable costs can be estimated from percentages of other cost estimations already achieved, see *Appendix C* for further details and calculations.

$$Annual\ production\ cost\ = \$2{,}334{,}076$$

$$Production\ cost\ (\$/tonne) = \$233$$

The oil that is extracted and can be used a feedstock for biodiesel production generates approximately $800 per ton. In addition to this the residual solid coffee grounds can be utilized as fuel pellets and has the potential to generate approximately $140 per ton. On a wet weight basis extraction percentage of 9% and assuming the moisture content of the coffee is 45%, the following calculation will estimate the profit made from selling the products.

$$Oil = (10{,}000 * 0.09) * 800$$

$$Oil = \$720{,}000.00$$

$$Fuel\ Pellets\ = (10{,}000 * 0.55) * 140$$

$$Fuel\ Pellets\ = \$770{,}00.00$$

$$Overall\ annual\ profit\ = \$1{,}490{,}000$$

With the overall revenue estimated it is now possible to calculate the profit by subtracting the annual production cost from the annual profit.

$$Profit\ = \$1{,}490{,}000 - \$2{,}334{,}076$$

$$Loss = \$844{,}076$$

The estimation suggests that this process would lose $844,076 would for every year of production. This assessment requires further investigation to provide a more accurate estimation.

6 Discussion & Recommendations

While a Dimethyl Ether extraction experiment has been performed, this was a once through semi-batch style process. This experiment did, however, provide valuable information about the system in relation to determining how much Dimethyl Ether is required for a specified amount of spent coffee grounds. One of the issues that were mentioned by a refrigeration mechanic was that the compressors in the refrigeration systems required lubrication in order for the compressor to operate. In conventional refrigeration systems an oil separator is located post compression, this removes the lubricating oil from the refrigerant and can be delivered back to the compressor via an oil level management system. Due to that fact that this process is extracting oil, it was advised that this system would require several oil separators throughout the process. This is not an easy aspect to design or economical for that matter, and without it there would be a contamination of lubricating oil in the extracted oil. One solution to this would be to use a compressor which did not require lubrication, such as a compressor which uses magnetic bearing technologies. This was not looked into in great depth due to the project having alternative stipulation but should be considered in any future work.

Another issue when designing a continuous extraction process was the ability to have a constant feed of fresh coffee grounds into the system without having to stop the process and refill the extraction vessel. Theoretically, this continuous feeder would fill the reactor at a rate where enough interaction is experienced between the Dimethyl Ether and coffee grounds to extract all the oil content. Further investigation and research must be conducted to prove the validity of this method.

Although the amount of Dimethyl Ether to coffee grounds has been determined, it is believed that this amount could be more than required. With a continuous extraction system which recycled the Dimethyl Ether via compression and condensation, like a vapor-compression refrigeration system, and returned it back into the storage vessel, this value could be reduced. This would also illustrate how much Dimethyl Ether is lost through evaporation which can then be modeled in Aspen. Furthermore, the effects of the temperature and extraction time have not been investigated for this process. The effect of temperature has a significant influence on the rate of extraction of crude lipids from biomass sources is anticipated to enhance extraction time. To optimize the extraction yield and reduce the amount of solvent used and extraction time, and hence reduce energy consumption, an investigation on the effects that temperatures have on the rate of extraction must also be performed. It should also be mentioned that although this work included a hexane process to separate the extracted oil, future investigation into a centrifuge process to separate the solvent and solid material from the extracted oil.

The results that have been generated by the Aspen model have identified some important information about how the process will perform with the extraction solvent Dimethyl Ether. By implementing the flow rate determined from a continuous extraction plant with a capacity of 10,000 tons per year, the operating conditions and requirements of the equipment was obtained. Although these results are important for the techno-economic assessment, it is hard to verify this data against any real experimentation data. Validation of data is very important when conducting an investigation into a potential alternative processing technique, and this situation is no different.

After the techno-economic assessment was conducted some interesting results were found. The procedure and computations of the assessment were based on the factorial estimation method

described in (Sinnot 2005). Although this method takes numerous factors into account, some of the costs that have been included are most probably not required by this particular process. This plant would only perform the extraction of oil from coffee grounds rather than the post processes to convert the oil into biodiesel, which requires quite a substantial amount of equipment, direct/indirect costs and operating expenses. Therefore, it is believed that a refined input of factors should be applied to enhance the economic outcome. With the experimental results anticipated from the design of a continuous system, the cost of raw materials is expected to be reduced. One of the most influential factors for the assessment was the total purchasing cost of the major equipment. With very limited time left while performing the assessment, the sizing of the equipment was not able to be done with great accuracy. This led to using some sizing and cost estimates that were presented in (Sinnot 2005) to calculate the respective components needed. To accomplish a detailed techno-economic assessment, further work is needed to accurately size the equipment to a greater degree. Overall, the results presented have shown that the length of time that would be required to see a return on the investment made is too great for the project to be considered a viable investment.

7 Conclusion

With vast amounts of research and development being conducted around the globe to provide advancements in current biodiesel processing technology, the economical downfall with existing feedstock's that have restricted biodiesel's range of applications still continue. It was the aim of this thesis report to investigate an alternative method of extracting oil from waste oil sources, in particular, spent coffee grounds. Through experimentation, model simulation, and a techno-economic assessment, this thesis report has revealed results which, in comparison to current extraction methods, have proven to be significant.

Aspen plus was employed to model the system and facilitate the design of the experiment. However, with the author's lack of experience modeling solids in Aspen plus and no existing literature on the subject available that was able to aid with the model development, the decision was made to obtain the outcomes from the experimental work prior to modeling. These results would then allow for a flow rate of Dimethyl Ether to be determined and implemented into the model.

After the initial design for a continuous system not going ahead due to issues identified by the refrigeration mechanics, a simplified 'once through' design was adopted and constructed. The outcome from the experiment work performed is this thesis has proven the feasibility of Dimethyl Ether as a potential solvent for the extraction of oil. With its inherent ability to simultaneously remove the moisture and oil content from the coffee grounds, Dimethyl Ether extraction is able to eliminate the excessive energy consumption required by drying the coffee grounds. Furthermore, with extraction yields from a system that is yet to be optimized exceeding or equaling that of current techniques, it is anticipated that the investigated extraction process could potentially replace conventional methods. The development of the experimental apparatus into a continuous process is required to prove the system can produce the same results when the vapor-compression feature is implemented.

The model that was implemented used the conceptual operating principles of a simple refrigeration process, namely, the thermodynamic vapor-compression cycle. With the results from the experiment applied into the Aspen model, energy and material balances were able to be calculated. Yet, with no means to validate these results it is hard to determine the feasibility of this data. To truly verify that this process can be possible on an industrial scale, further development of the model is essential.

One of the requirements of this thesis report was to evaluate the economic potential of the investigated system. A techno-economic assessment was performed in order to determine the feasibility of a full scale processing plant. With the results from this not conforming to what was expected, it is believed that with the results anticipated from further developed experiment and Aspen model the feasibility of the process can be proven. Along with the optimization of the system, the possibility to either utilize or sell the refrigeration energy dissipated from the expansion of Dimethyl Ether could significantly influence the economic assessment. The comparison of these results to current extraction plants could then be made to identify the ability to replace conventional methods.

8 Future Work

8.1 Introduction

This section describes some of the aspects of this project which need further development and research. This includes designing a continuous system that will integrate the vapor-compression cycle into the experiment, enabling important information about the process to be obtained with greater accuracy. Further work on the GC-MS analysis is required to accurately compare and identify retention times of the different methyl esters present in the oil extracted. Also, development of an Aspen Plus model that will incorporate the extraction of oil from coffee grounds, flash evaporation/separation of the Dimethyl Ether, oil and water mixture and sensitivity analysis on operating conditions. These advancements would also facilitate a detailed techno-economic assessment to be performed, rather than a preliminary one, with a comparison to current extraction technologies.

8.2 Experimental Work

8.2.1 Continuous System Experiment Design

With the aid of refrigeration mechanics and further research into the process requirements, a continuous process experiment needs to be designed and constructed. This would include the additional of a continuously fed extraction vessel, condenser, compressor, heat exchanger and flash/separation vessel. This process would then operate as a vapor-compression refrigeration cycle while simultaneously performing extraction.

8.2.2 Continuously Fed Extraction Vessel

Brief investigation into how a continuously fed extraction vessel could be designed for this process, but many of the technologies found by the author, while saying they were continuous, still operated as semi-batch process. The design of this vessel is not an easy task due to the solvent being used. At atmospheric pressure Dimethyl Ether is a gas, having a boiling point of -24°C. This means that the extraction vessel has to been completely enclosed, eliminating any drop in pressure during extraction. Coffee grounds need to be continuously fed and removed from the vessel without exposing the Dimethyl Ether to atmospheric pressure, otherwise the liquefied Dimethyl Ether will vaporize during extraction and hence increase the amount of solvent required. Future investigation and research must be conducted in order to achieve such a design.

8.2.3 Flash/Separation Drum

A flash evaporation vessel commonly referred to as a flash drum or something which can perform the same flash/separation functionality must be implemented into the design to achieve continuous operation. This unit will enable the liquefied Dimethyl Ether to vaporize and separate from the extracted oil and water. This oil and water could then be removed by and outlet valve. Investigation into technologies or current products that can achieve this must be conducted to produce a system which can function to the desired operation.

8.2.4 Compressor

To design a process that will operate like that of a refrigeration system, a compressor needs to be implemented into the design. On a bench scale, only a small compressor would be necessary but it needs to capable of handling a flammable substance. With flammable refrigerants currently used in the air conditioning and refrigeration systems, there are products available. However, as mentioned

in the conclusion, the compressors require lubrication (oil). There are two possible options in order to achieve this. One could be to, and not the desired option, use an oil separator in the system with an oil level management device to redeliver the oil but this would also result in contamination of the desired oil extracted from the coffee grounds. The alternative would be to investigate the use of a compressor which uses magnetic bearing technology that eliminates the need for lubrication. Future work must be conducted to investigate the most economical and efficient option.

8.2.5 Condenser

The compression stage of this process will make the Dimethyl Ether experience an increase the temperature of due to its rise in pressure. This superheated vapor that will exit from the compressor needs to be condensed in order to be fed back into the extraction vessel. This can be achieved by a water cooled condenser which will remove any superheat from the Dimethyl Ether vapor as it travels through the condenser. A bench scale condenser needs to be purchased that will meet the heat rejection requirements of the system.

8.2.6 Heat Exchanger

With the addition of the flash/separation vessel this unit is not essential for the design of the continuous experiment. However, due to the amount of cooling energy dissipated by the expansion of Dimethyl Ether, an indication of the possible use of this energy to perform refrigeration could be studied. If this utilization of energy can be used to cool other areas of the facility or potentially sold as refrigeration, this could reduce the operating costs of the process and even contribute to the profit. In order to achieve the most efficient transfer of this energy, future investigation should be made to select the best suited type of heat exchanger for this application.

8.2.7 Investigation of Temperature

Future investigation into the effect temperature has on the rate of extraction in essential to optimize the process. By adding the capability to control the operating temperature of the extraction and observe the influence it has on the system, it would then be possible to re-evaluate the amount of Dimethyl Ether required. This would result in a lower solvent flow rate and hence reduce the cost of raw materials from an economical point of view. Furthermore, if the influence of temperature was known, this could increase the rate of extraction and possibly the level of extraction resulting in higher extraction yields for shorter processing time. Forthcoming work is required to integrate this functionality in to the design.

8.2.8 GC-MS Analysis

To accurately identify and verify the methyl esters present in the oil obtained from the spent coffee grounds extraction experiments, further GC-MS work is required. Future work for this aspect of the project would require developing a superior GC-MS method by experimenting with the operating conditions of the system. Once this was accomplished the FAME standards could be run through multiple times to ensure that the retention times constituents for the different methyl esters are accurate. Thus, enabling the verification of retention times for the methyl esters present in the C17 spiked esterified oil samples that were collected from the experiments. This would provide the ability to compare the quality and characteristics of oil extracted by the Dimethyl Ether extractions to that reported in the relative literature and also identify if the oil meets the requirements to produce biodiesel.

8.3 Aspen plus Model

As mentioned previously, a continuous extraction experiment needs to be designed and constructed, similar to that illustrated in Figure 12. The data that would be obtained from this experiment would greatly enhance the modeling accuracy. In terms of the flow rate of Dimethyl Ether required to extract a known amount of coffee grounds, the continuous experiment would improve the flow rate of solvent necessary. Once this was determined, the material and energy balances generated by the Aspen model could be optimized to achieve the most efficient results and reduce the operating costs of the process. In turn, this would then re-evaluate the amount of heat absorbed and rejected by the condenser and evaporator and also power requirements of the compressor. By implementing this information into the Aspen model, sizing of the equipment would be done with a greater accuracy.

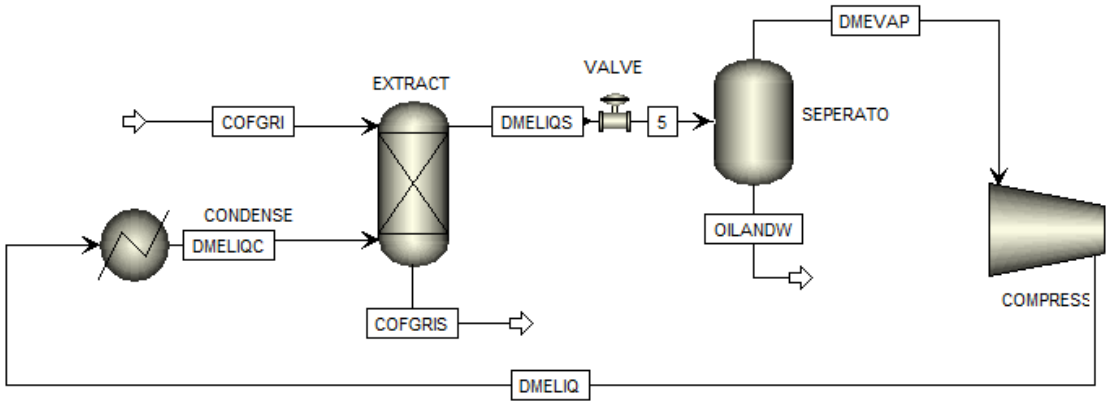

Figure 11 - Future Aspen Model Design

Another important aspect to the Aspen model which needs further development is the flash evaporation unit or flash drum. The Aspen model demonstrated in this project achieved simulation of the flash drum by using a heat exchanger. Although an energy balance was obtained from this, a model implementing a flash drum would produce results with a greater degree of accuracy in terms of the degree of separation. The extracted moisture (water) and oil from the spent coffee grounds is contained in the liquefied Dimethyl Ether. Once this mixture has experienced the pressure drop across the thermal expansion valve, the saturated Dimethyl Ether partially vaporizes from the oil and water. To determine and optimize this stage of the process, an Aspen model including a flash drum unit should be explored.

A fundamental aspect of this Aspen model is to simulate a continuous process; this includes an extraction vessel that has a coffee grounds feed rate. Solid modeling in Aspen plus for a compound as complex as coffee is also difficult due to there being a lack of published work on this process.

Furthermore, after conducting physical experiments on the influence that temperature has on the rate of extraction, a sensitivity analysis could be performed on both the feed rate of coffee grounds and operation temperature. This information would have a significant impact of the techno-economical assessment. The future work on the model that has been discussed needs to be developed, with the aid of a continuous system design, to not only refine the process in terms of extraction but also from an economical point of view.

8.4 Techno-economic Assessment

The incorporation of the following aspects need to considered for the future development of the techno-economic assessment. Through the data that will be obtained from a continuous experiment and complete Aspen model, the estimation of refrigeration energy produced by the system can be obtained. Investigation into how this could be utilized within the plant facility or even the possibility too vend this energy could dramatically alter the outcome of the assessment. Another economical aspect is the logistical costs to transport all the spent coffee grounds available into one central processing location. The exploration into this would require vast amounts of research to accurately determine. A thorough comparison to conventional extraction plants is also essential for the economical validity to be proven.

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10 Appendix A - Experiment calculations

10.1 Hexane

10.1.1 Experiment one

- Time started 9.42am
- Time finished 10.35am
- Experiment duration – 53 minutes
- Thimbles filled = 14
- Weight of SCG (BE) – 25g
- Weight of SCG (AE) – 21.694g
- Percentage of oil = $\frac{25-21.694}{25} * 100 = 13.224\%$
- Weight of flask = 72.654
- Weight of flask with pure oil = 75.597
- Oil Extracted = $75.597 - 72.654 = 2.943g$

10.1.2 Experiment Two

- Time started 10.01am
- Time finished 11.18am
- Experiment duration – 1 h and 17 minutes
- Thimbles filled = 19
- Weight of SCG (BE) – 25g
- Weight of SCG (AE) – 22.285g
- Percentage of oil = $\frac{25-22.285}{25} * 100 = 10.86\%$
- Weight of flask = 80.850
- Weight of flask with pure oil = 83.554
- Oil Extracted =$83.554 - 80.850 = 2.704g$

10.2 Dimethyl Ether Extraction

10.2.1 Experiment One

10.2.1.1 Coffee Sample

- 211.8g of coffee was placed inside the steel canister.

10.2.1.2 Dimethyl Ether Used

- Before Extraction - 14.2 kg
- After Extraction - 10.6 kg
- DME Used - 14.2 – 10.6 = 3.6 kg

10.2.1.3 Pressure

- 420 kPa

10.2.1.4 Oil Recovery

- Round bottom flask = 90.378 g
- RBF with oil = 107.928 g
- $Oil\ Recovery \rightarrow 107.928 - 90.378 = 17.55\ g$
- %Oil in SCG on a dry weight basis (DWB)
- $\frac{17.55}{(211.8*(1-0.46238))} = 15.41\%\ Oil\ Content$

10.2.1.5 After Extraction

- $Residual\ SCG \rightarrow 211.8 - 96.316 = 115.484\ g$

10.2.1.6 Moisture Content of SCG sample via experiment

- Moisture Content $= \frac{97.934g}{211.8g} * 100 = 46.238\%$

10.2.2 Experiment Two

10.2.2.1 Coffee Sample

- 204.909g of coffee was placed inside the steel canister.

10.2.2.2 Dimethyl Ether Used

- Before Extraction - 19.8 kg
- After Extraction -14.4 kg
- DME Used - 19.8 – 14.4 = 5.4 kg

10.2.2.3 Pressure

- 420 kPa

10.2.2.4 Oil Recovery

- Round bottom flask = 111.122 g
- RBF with oil = 128.334 g
- $Oil\ Recovery \rightarrow 128.334 - 111.112 = 17.22\ g$
- %Oil in SCG on a dry weight basis (DWB)
- $\frac{17.22}{(204.909*(1-0.42619))} = 14.64\%\ Oil\ recovery$

10.2.2.5 After Extraction

- $Residual\ SCG \rightarrow 204.909 - 100.358 = 104.551\ g$

10.2.2.6 Moisture Content of SCG

- Moisture Content $= \frac{87.331g}{204.909g} * 100 = 42.619\%$

11 Appendix B - Aspen Plus Model Result tables

11.1 Compressor

Compressor model:	Isentropic Compressor	
Phase calculations:	Vapor phase calculation	
Indicated horsepower:	795.026	kW
Brake horsepower:	795.026	kW
Net work required:	795.026	kW
Power loss:	0	kW
Efficiency:	0.72	
Mechanical efficiency:	1	
Outlet pressure:	5.41325	bar
Outlet temperature:	59.7915	C
Isentropic outlet temperature	39.7814	C
Vapor fraction:	1	
Displacement:		
Volumetric efficiency:		

Figure 12 - Compressor Results

	FEVAP	FCOMP	
Substream: MIXED			
Mole Flow kmol/hr			
DIMET-01	557.576	557.576	
Total Flow kmol/hr	557.576	557.576	
Total Flow kg/hr	25687	25687	
Total Flow cum/hr	11046.9	2656.46	
Temperature C	-24.872	59.7915	
Pressure bar	1.01325	5.41325	
Vapor Frac	1	1	
Liquid Frac	0	0	
Solid Frac	0	0	
Enthalpy kcal/mol	-44.7608	-43.5348	
Enthalpy kcal/kg	-971.603	-944.99	
Enthalpy Gcal/hr	-24.9576	-24.274	
Entropy cal/mol-K	-59.9702	-58.907	
Entropy cal/gm-K	-1.30175	-1.27867	
Density kmol/cum	0.0504734	0.209894	
Density kg/cum	2.32526	9.66962	
Average MW	46.069	46.069	
Liq Vol 60F cum/hr	39.1594	39.1594	

Figure 13 - Compressor Stream Results

11.2 Condenser

Outlet temperature:	21.9996	C
Outlet pressure:	5.41325	bar
Vapor fraction:	1	
Heat duty:	-1496.28	MJ/hr
Net duty:	-415.632	kW
1st liquid / Total liquid:		
Pressure-drop correlation parameter:		

Figure 14 - Condenser Results

	FCOMP	FCOND	
Substream: MIXED			
Mole Flow kmol/hr			
DIMET-01	557.576	557.576	
Total Flow kmol/hr	557.576	557.576	
Total Flow kg/hr	25687	25687	
Total Flow cum/hr	2656.46	2279.74	
Temperature C	59.7915	21.9996	
Pressure bar	5.41325	5.41325	
Vapor Frac	1	1	
Liquid Frac	0	0	
Solid Frac	0	0	
Enthalpy kcal/mol	-43.5348	-44.1757	
Enthalpy kcal/kg	-944.99	-958.903	
Enthalpy Gcal/hr	-24.274	-24.6313	
Entropy cal/mol-K	-58.907	-60.9494	
Entropy cal/gm-K	-1.27867	-1.323	
Density kmol/cum	0.209894	0.244579	
Density kg/cum	9.66962	11.2675	
Average MW	46.069	46.069	
Liq Vol 60F cum/hr	39.1594	39.1594	

Figure 15 - Condenser Stream Results

11.3 Evaporator

Outlet temperature:	-24.872	C
Outlet pressure:	1.01325	bar
Vapor fraction:	1	
Heat duty:	-1365.82	MJ/hr
Net duty:	-379.394	kW
1st liquid / Total liquid:		
Pressure-drop correlation parameter:		

Figure 16 - Evaporator Results

	FVALVE	FEVAP	
Substream: MIXED			
Mole Flow kmol/hr			
DIMET-01	557.576	557.576	
Total Flow kmol/hr	557.576	557.576	
Total Flow kg/hr	25687	25687	
Total Flow cum/hr	12880.8	11046.9	
Temperature C	13.7266	-24.872	
Pressure bar	1.01325	1.01325	
Vapor Frac	1	1	
Liquid Frac	0	0	
Solid Frac	0	0	
Enthalpy kcal/mol	-44.1757	-44.7608	
Enthalpy kcal/kg	-958.903	-971.603	
Enthalpy Gcal/hr	-24.6313	-24.9576	
Entropy cal/mol-K	-57.7813	-59.9702	
Entropy cal/gm-K	-1.25423	-1.30175	
Density kmol/cum	0.0432873	0.0504734	
Density kg/cum	1.99421	2.32526	
Average MW	46.069	46.069	
Liq Vol 60F cum/hr	39.1594	39.1594	

Figure 17 - Evaporator Stream Results

11.4 Expansion valve

Choking status:	Choking is not checked	
Outlet pressure:	1.01325	bar
Pressure drop:	4.4	bar
Choked outlet pressure:		
Outlet temperature:	13.7266	C
Outlet vapor fraction:	1	
Valve flow coefficient:		
Valve % opening:		
Cavitation index:		
Pressure drop ratio factor:		
Pressure recovery factor:		
Piping geometry factor:	1	

Figure 18 - Expansion Valve Results

	FCOND	FVALVE	
Substream: MIXED			
Mole Flow kmol/hr			
DIMET-01	557.576	557.576	
Total Flow kmol/hr	557.576	557.576	
Total Flow kg/hr	25687	25687	
Total Flow cum/hr	2279.74	12880.8	
Temperature C	21.9996	13.7266	
Pressure bar	5.41325	1.01325	
Vapor Frac	1	1	
Liquid Frac	0	0	
Solid Frac	0	0	
Enthalpy kcal/mol	-44.1757	-44.1757	
Enthalpy kcal/kg	-958.903	-958.903	
Enthalpy Gcal/hr	-24.6313	-24.6313	
Entropy cal/mol-K	-60.9494	-57.7813	
Entropy cal/gm-K	-1.323	-1.25423	
Density kmol/cum	0.244579	0.0432873	
Density kg/cum	11.2675	1.99421	
Average MW	46.069	46.069	
Liq Vol 60F cum/hr	39.1594	39.1594	

Figure 19 - Expansion Valve Results

Appendix C - Techno-Economic Calculations

1.1 Equipment calculations (Sinnot 2005)

$$Compressor - C_e = 1920 \times 796^{0.8}$$

$$Compressor - C_e = \$401{,}820.12$$

$$Condenser - C_e = bare\ cost * type\ factor * pressure\ factor$$

$$Condenser - C_e = 20{,}000 * 0.8 * 1.1$$

$$Condenser - C_e = \$17{,}600.00$$

$$Heat\ Exchanger - C_e = bare\ cost * type\ factor * pressure\ factor$$

$$Heat\ Exchanger - C_e = 20{,}000 * 0.8 * 1.0$$

$$Heat\ Exchanger - C_e = 16{,}000.00$$

$$Solvent\ Tank - C_e = 1400 \times 35^{0.55}$$

$$Solvent\ Tank - C_e = \$9893.85$$

$$Separation\ Vessel - C_e = 15{,}000 \times 35^{0.4}$$

$$Separation\ Vessel - C_e = \$62{,}189.00$$

$$PCE = 401{,}820.12 + 17{,}600.00 + 16{,}000.00 + 9893.85 + 62{,}189.00$$

$$PCE = \$507{,}503$$

Table 6 - Equipment Factors (Sinnot 2005)

Equipment	Size	Size range	Constant $	Index
Compressor	kW	796	1920.00	0.8
Separation Vessel	M^3	35	15,000.00	0.4
Solvent Tank	M^3	35	1400.00	0.55
Heat Exchanger	M^2	379	20,000.00	0.8
Condenser	M^2	417	20,000.00	0.8

Table 6.6. Summary of production costs

Variable costs	*Typical values*
1. Raw materials	from flow-sheets
2. Miscellaneous materials	10 per cent of item (5)
3. Utilities	from flow-sheet
4. Shipping and packaging	usually negligible
Sub-total A	.....
Fixed costs	
5. Maintenance	5–10 per cent of fixed capital
6. Operating labour	from manning estimates
7. Laboratory costs	20–23 per cent of 6
8. Supervision	20 per cent of item (6)
9. Plant overheads	50 per cent of item (6)
10. Capital charges	10 per cent of the fixed capital
11. Insurance	1 per cent of the fixed capital
12. Local taxes	2 per cent of the fixed capital
13. Royalties	1 per cent of the fixed capital
Sub-total B	.....
Direct production costs A + B	.....
13. Sales expense	20–30 per cent of the direct
14. General overheads	production cost
15. Research and development	
Sub-total C	.....
Annual production cost = A + B + C =	.....
Production cost £/kg = $\frac{\text{Annual production cost}}{\text{Annual production rate}}$	

Figure 20 - Summary of Production Costs (Sinnot 2005)

$$Total\ Utility\ costs\ = \$61{,}264$$

$$Operating\ Labor = \$240{,}000$$

$$Maintenance = \$111{,}904$$

$$Miscellaneous\ materials = \$11{,}190$$

$$Laboratory\ costs = \$48{,}000$$

$$Supervision = \$48{,}000$$

$$Plant\ overheads = \$120{,}000$$

$$Capital\ charges = \$223{,}809$$

$$Insurance\ = \$22{,}380$$

$$Local\ Taxes = \$44{,}761$$

$$Royalties = \$22{,}380$$

$$Annual\ production\ cost\ = \$1{,}208{,}542$$

$$Production\ cost\ (\$/kg) = \$120.85$$